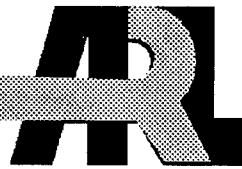


ARMY RESEARCH LABORATORY



Investigation of the Characteristics of Ferroelectric Thin Films Deposited By Pulsed Laser Ablation

S. Sengupta, N. Sonnenberg, D.P. Vijay, and S.B. Desu

ARL-TR-682

December 1994



19950320 109

Approved for public release; distribution unlimited.

DTIC QUALITY INSPECTED 1

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Citation of manufacturer's or trade names does not constitute an official endorsement or approval of the use thereof.

Destroy this report when it is no longer needed. Do not return it to the originator.

Contents

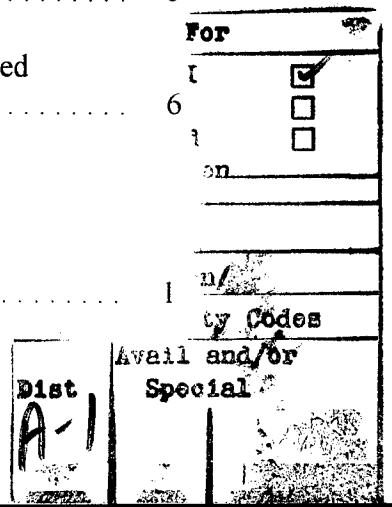
	Page
Introduction	1
Experimental	1
Results and Discussion	
Glancing Angle X-ray Results	2
Electronic Measurements	3
Conclusions	6
Acknowledgments	6
References	6

Figures

1(a). Glancing angle x-ray diffraction pattern of undoped BSTO film deposited on MgO. Oxygen partial pressure = 50 mT. Inset shows x-ray pattern of the target material	3
1(b). Glancing angle x-ray diffraction pattern of undoped BSTO film deposited on LaAlO ₃ . Oxygen partial pressure = 50 mT. Inset shows x-ray pattern of the target material	4
2(a). Glancing angle x-ray diffraction pattern of undoped BSTO film deposited on RuO ₂ /Sapphire. Oxygen partial pressure = 150 mT	4
2(b). Glancing Angle X-ray diffraction pattern of undoped BSTO film deposited on RuO ₂ /Sapphire. Oxygen partial pressure = 50 mT	5
3. Capacitance versus Voltage characteristics of BSTO thin film deposited on RuO ₂ /Sapphire. P _{Oxygen} = 150 mT	5
4. Capacitance versus Voltage characteristics of the BSTO thin film deposited on RuO ₂ /Sapphire. P _{Oxygen} = 50 mT	5

Tables

1. Lattice Parameters and Dielectric Constants for MgO, Al ₂ O ₃ and LaAlO ₃ Substrates
--



INTRODUCTION

A ceramic Barium Strontium Titanate, $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$, phase shifter using a planar microstrip construction has been demonstrated.¹ In order to obtain higher operating frequencies (beyond 30 GHz) and to decrease the voltage requirements, thin film fabrication of the above candidate materials is necessary. The electronic characteristics of BSTO and oxide-modified BSTO films have already been demonstrated.^{2,3}

In this work, we have investigated the effect of the thin film stoichiometry on electrical performance by measuring the dielectric constants and tunability in the low frequency (KHz) range. A HP 4194A impedance analyzer was used for these measurements. The results of these measurements will be discussed.

EXPERIMENTAL

The lattice parameters and dielectric constants of the substrates used in these experiments are listed in Table 1. Prior to Pulsed Laser Deposition (PLD), the substrates underwent a cleaning process that included an ultrasonic cycle in TCE followed by two methanol ultrasonic cycles. The samples were then rinsed with methanol and air dried.

TABLE I. Lattice Parameters and Dielectric Constants for MgO , Al_2O_3 and LaAlO_3 Substrates.

	SUBSTRATE		
	<u>MgO</u>	<u>Al_2O_3</u>	<u>LaAlO_3</u>
Lattice Parameter (\AA)	4.21	4.76	3.79
Dielectric Constant (300K)	10	11	23

The ceramic ablation target chosen for this work was $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ (BSTO). In order to measure the electronic properties of the films, a ground plane electrode of Ruthenium oxide (RuO_2) was sputtered onto the substrates at a substrate temperature of 200 °C and a O_2/Ar ratio of 1:4 with a total pressure of 10 mT. The Ruthenium oxide films were 3000 Å thick. The thickness measurement was performed using a Dektak-200 profilometer. The resistivity of the as-deposited films was on the order of 160 $\mu\text{ohms}\cdot\text{cm}$. These were annealed at 600 °C for 30 minutes to lower the resistivity and then cooled by furnace quenching. The resistivity of the annealed films was measured to be 110 $\mu\text{ohms}\cdot\text{cm}$.

The PLD was accomplished using a Questek 2000 krypton-fluoride excimer laser with a wavelength of 248 nm and a repetition rate of 10 Hz. The substrate was parallel to the target with a separation distance of 55 mm. The average pulse energy was 300 mJ with a 20 ns pulse width. The substrate temperature was 500 °C, as monitored by a thermocouple clamped between the heater and the substrate. The powder pressed ceramic targets were prepared according to a

description published previously.² The oxygen partial pressures used for this experiment were 150 mT or 50 mT. A Dektak-200 profilometer was used to measure the film thickness that was approximately 6000 Å on all the substrates.

The thicknesses of the top Pt electrodes were measured to be approximately 3000 Å also using profilometry. The metallized films used for the electrical measurements consisted of Sapphire/RuO₂/BSTO / Pt. Thin films of BSTO were also deposited on bare substrates of MgO and LaAlO₃.

The glancing angle x-ray measurements were performed using a Rigaku RU 200 rotating anode x-ray diffractometer. The entrance slit had a width of 0.2° and the angle of incidence of the Cu K α ($\lambda=1.5415$ Å) beam was set at 1°. The step scanning interval was 0.02° and the scan rate was 5°/minute.

The dielectric constant (ϵ') and % tunability were determined for all thin film/substrate combination. The % tunability of a material is determined using the following equation:

$$\% \text{ tunability} = \{ \epsilon'(0) - \epsilon'(V_{app}) \} / \{ \epsilon'(0) \} \quad (1)$$

The tunability measurements were taken with an applied electric field which ranged from 0 to +/- 2.0 V/micron (μm). The electronic properties were measured using a 30 KHz frequency. Capacitance versus voltage (C-V) measurements for the films were taken using an HP4194 impedance / phase gain analyzer. The voltage, applied internally through the HP 4194A, was varied from -1.2 V to +1.2 V.

RESULTS AND DISCUSSION

Glancing Angle X-ray Results

The glancing angle x-ray diffraction patterns (GAXRD) for the undoped BSTO thin films deposited on MgO and LaAlO₃ are shown in Figures 1(a) and 1(b). Both the films were deposited under a oxygen partial pressure of 50 mT using the same ceramic ablation target. As shown in the figures, the GAXRD gives evidence of the existence of a secondary phase (Ba_{0.91}Sr_{0.09}TiO₄) in the thin films whereas, the x-ray diffraction pattern of the target (inset) does not show the presence of this secondary phase.

In order to examine the role of the type of oxide bottom contact layer, the undoped thin films were also deposited on RuO₂/sapphire substrates. Figures 2(a) and 2(b) show the GAXRD of undoped BSTO thin films deposited on RuO₂/sapphire substrates under the oxygen partial pressures of 150 mT and 50 mT. The GAXRD does not indicate the presence of the same secondary phase (Ba_{0.91}Sr_{0.09}TiO₄) when the film was deposited under a partial pressure of 150 mT on the RuO₂/sapphire substrate but the secondary phase was present for the 50 mT sample. It is important to note that the same BSTO ceramic ablation target was used for all the thin film depositions shown in Figures 1(a), 1(b), 2(a), and 2(b).

Electronic Measurements

Fig. 3 shows the capacitance versus voltage characteristics for the undoped BSTO film deposited on RuO₂/Sapphire (P_{oxygen} = 150 mT) measured at 30 KHz. The dielectric constant at a zero bias was about 1470 with a tunability of about 40% at a field of 2.0 V/μm. The curve shows a symmetric capacitance-voltage relationship which is characteristic of paraelectric films. Figure 4 shows the C-V curve for the undoped BSTO film deposited on RuO₂/sapphire deposited at a partial pressure of 50 mT also measured at 30 KHz. A dielectric constant of 1280 and a tunability of 48 % (V_{applied} = 2.0 V/μm) was obtained. A dielectric constant of 940 and a tunability of 55% (V_{applied} = 3.3 V/μm) were obtained for the same thin film at 0.5 MHz.

It is evident that the tunability of the film is not significantly altered at the two frequencies (30 KHz and 0.5 MHz) due to the presence of a secondary phase. Also, the dielectric constant and the tunability of the two BSTO films deposited under different oxygen partial pressures seem to be within acceptable range (< 15%) of each other. Also, any porosity and/or leakage current in the films will tend to alter the dielectric constants obtained. The bulk form of the undoped material has a dielectric constant of 3300 and a tunability of 20 % at 0.73 V/μm.

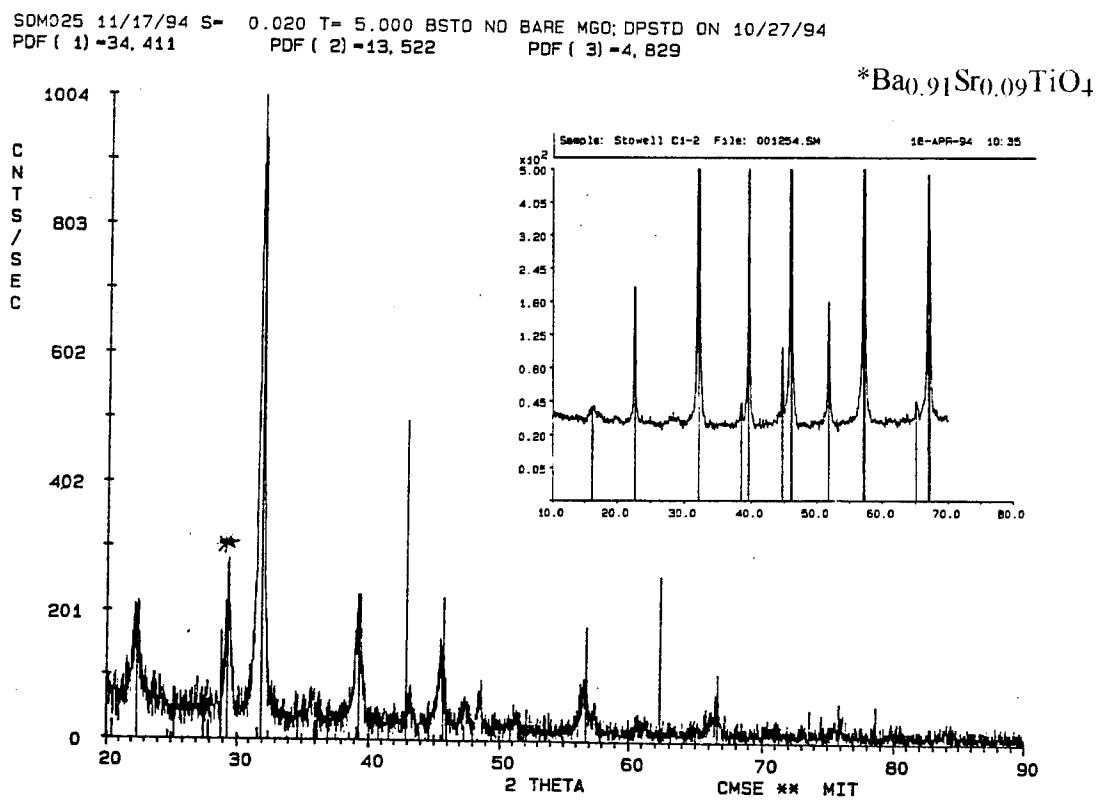


Fig. 1(a). Glancing angle x-ray diffraction pattern of undoped BSTO film deposited on MgO. Oxygen partial pressure = 50 mT. Inset shows x-ray pattern of the target material.

SDM026 11/17/94 S= 0.020 T= 5.000 BSTO ON BARE LAAL03; DPSTD ON 10/27/94
 PDF (1)=34, 411 PDF (2)=13, 522 PDF (3)=31, 22

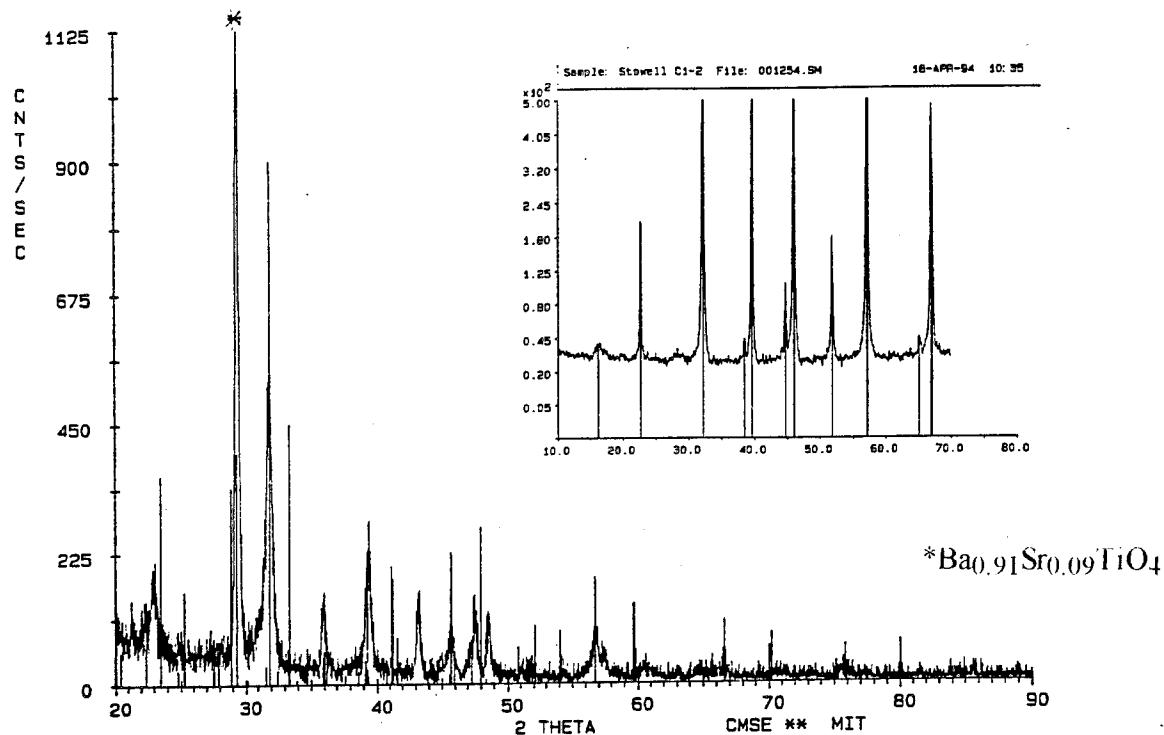


Fig. 1(b). Glancing angle x-ray diffraction pattern of undoped BSTO film deposited on LaAlO₃. Oxygen partial pressure = 50 mT. Inset shows x-ray pattern of the target material.

SDM024 11/17/94 S= 0.020 T= 5.000 BSTO/RUO2/SAFIR; SAMPLE A
 PDF (1)=34, 411 PDF (2)=21, 1172 PDF (3)=4, 802 PDF (4)=13, 522
 PDF (5)=10, 173

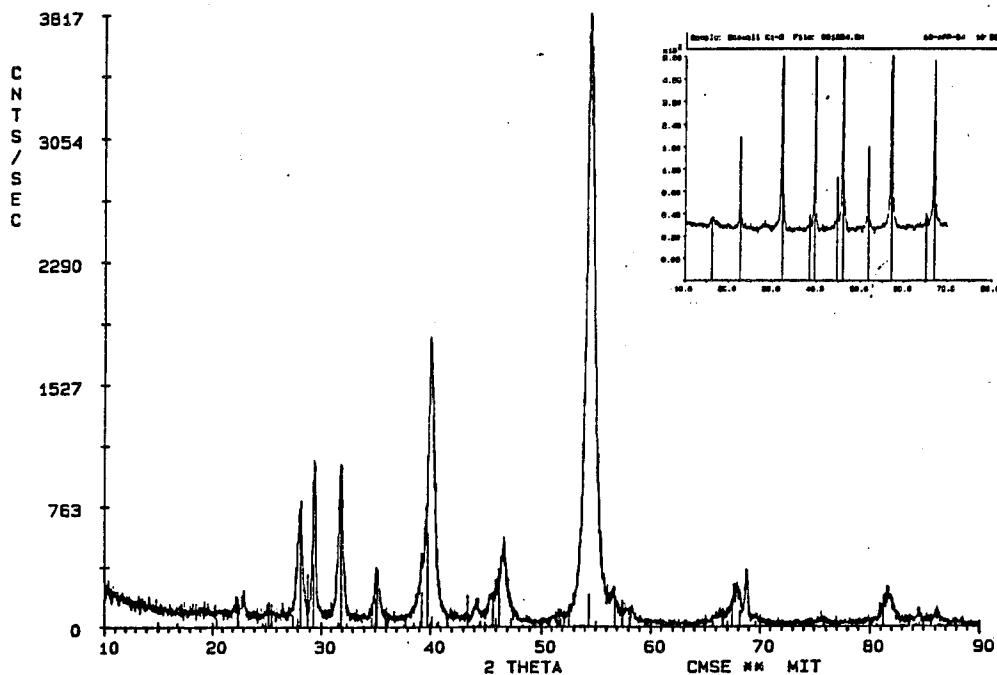


Fig. 2(a). Glancing angle x-ray diffraction pattern of undoped BSTO film deposited on RuO₂/Sapphire. Oxygen partial pressure = 150 mT.

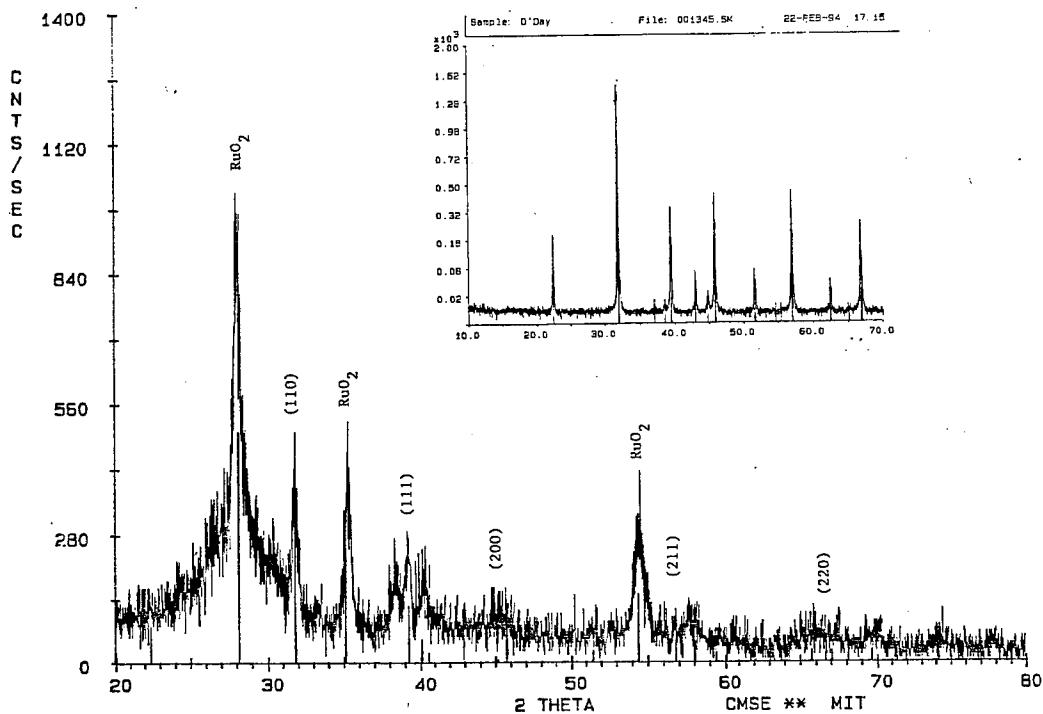


Fig. 2(b). Glancing Angle X-ray diffraction pattern of undoped BSTO film deposited on RuO₂/Sapphire. Oxygen partial pressure = 50 mT. The broadening of the peaks are attributed to the inherent noise level of the GAXRD system.

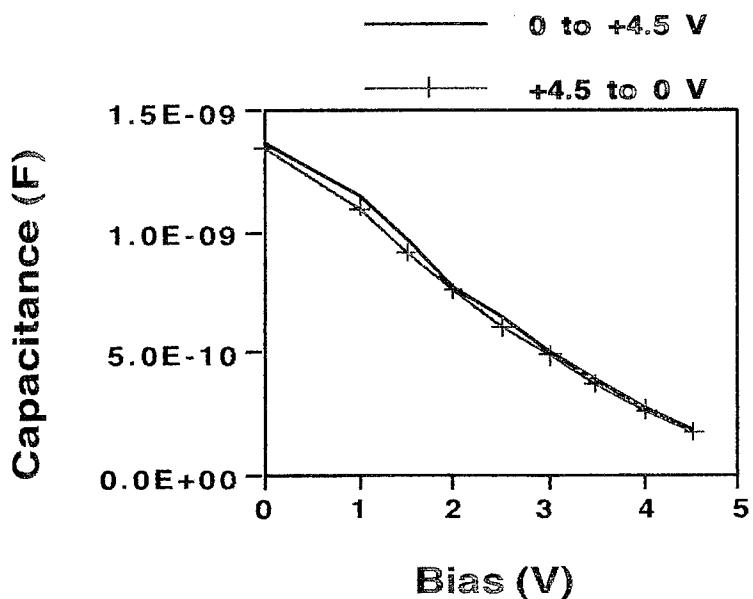


Fig. 3. Capacitance versus Voltage characteristics of BSTO thin film deposited on RuO₂/Sapphire. P_{oxygen} = 150 mT.

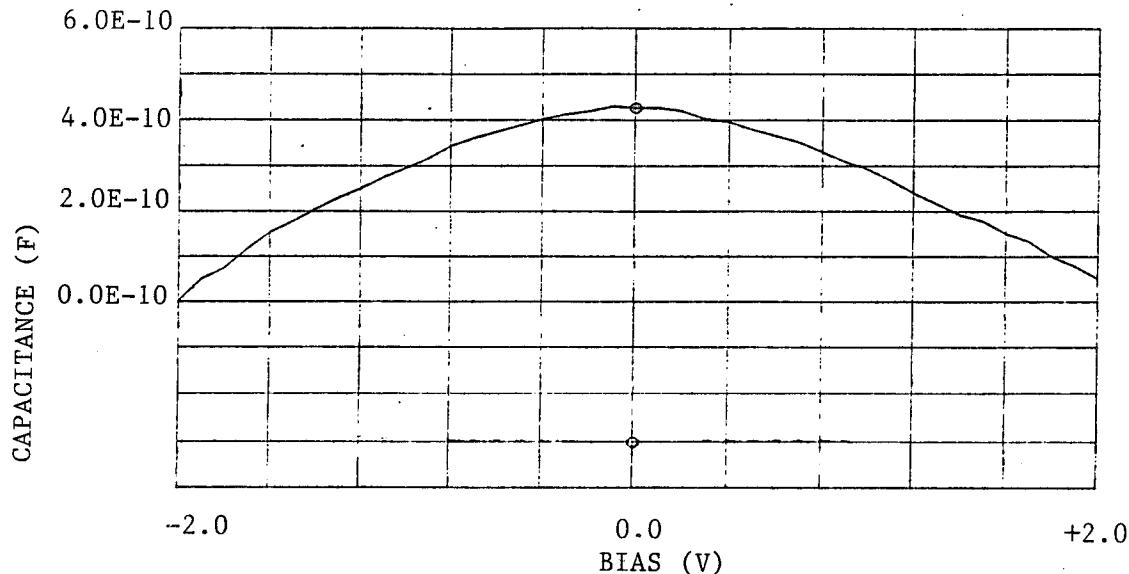


Fig. 4. Capacitance versus Voltage characteristics of the BSTO thin film deposited on RuO₂/Sapphire. P_{oxygen} = 50 mT.

CONCLUSION

It has been demonstrated that the presence of a small amount of secondary phase in the BSTO thin film may not significantly alter the electrical characteristics of the thin film. Establishing the percentage of a secondary phase that may alter its performance is under investigation using relative peak height ratios from GAXRD studies. The ongoing study will establish the tolerance factor for the composition and processing variations of a BSTO thin film for a particular device application. Similar investigations for oxide modified BSTO thin films is also underway.

ACKNOWLEDGMENTS

The authors would like to thank Allen Kirkpatrick of Epion Corporation, Bedford, MA for his help with the PLD.

REFERENCES

1. L.C. Sengupta, S. Stowell, E. Ngo, M.E. O'Day, and R. Lancto, *J. of Integrated Ferroelectrics*, (1994), in press.
2. R.Babbitt, T. Koscica, W. Drach, and D. Didomenico, *J. of Integrated Ferroelectrics*, (1994), in press.
3. S.Sengupta, L.C.Sengupta, S.Stowell, W.E.Kosik, E.Ngo, D.K.Vijay, and S.B.Desu, IEEE Transactions of the Proceedings of ISAF '94 (in press).

DISTRIBUTION LIST

No. of Copies	To
1	Office of the Under Secretary of Defense for Research and Engineering, The Pentagon, Washington, DC 20301
1	Director, U.S. Army Research Laboratory, 2800 Powder Mill Road, Adelphi, MD 20783-1197
1	ATTN: AMSRL-OP-SD-TP, Technical Publishing Branch
1	AMSL-OP-SD-TA, Records Management Administrator
1	Director, U.S. Army Research Laboratory, 2800 Powder Mill Road, Adelphi, MD 20783-1197
1	ATTN: Technical Library
2	Commander, Defense Technical Information Center, Cameron Station, Building 5, 5010 Duke Street, Alexandria, VA 23304-6145
1	ATTN: DTIC-FDAC
1	MIA/CINDAS, Purdue University, 2595 Yeager Road, West Lafayette, IN 47905
1	Commander, Army Research Office, P.O. Box 12211, Research Triangle Park, NC 27709-2211
1	ATTN: Information Processing Office
1	Commander, U.S. Army Materiel Command, 5001 Eisenhower Avenue, Alexandria, VA 22333
1	ATTN: AMCSCI
1	Commander, U.S. Army Materiel Systems Analysis Activity, Aberdeen Proving Ground, MD 21005
1	ATTN: AMXSY-MP, H. Cohen
1	Commander, U.S. Army Missile Command, Redstone Arsenal, AL 35809
1	ATTN: AMSMI-RD-CS-R/Doc
2	Commander, U.S. Army Armament, Munitions and Chemical Command, Dover, NJ 07801
2	ATTN: Technical Library
1	Commander, U.S. Army Natick Research, Development and Engineering Center, Natick, MA 01760-5010
1	ATTN: DFAS-IN-EM-TL, Technical Library
1	Commander, U.S. Army Satellite Communications Agency, Fort Monmouth, NJ 07703
1	ATTN: Technical Document Center
1	Commander, U.S. Army Tank-Automotive Command, Warren, MI 48397-5000
1	ATTN: AMSTA-ZSK
1	AMSTA-TSL, Technical Library
1	Commander, White Sands Missile Range, NM 88002
1	ATTN: STEWS-WS-VT
1	President, Airborne, Electronics and Special Warfare Board, Fort Bragg, NC 28307
1	ATTN: Library

No. of Copies	To
	Director, U.S. Army Research Laboratory, Weapons Technology, Aberdeen Proving Ground, MD 21005-5066
1	ATTN: AMSRL-WT
	Commander, Dugway Proving Ground, UT 84022
1	ATTN: Technical Library, Technical Information Division
	Commander, U.S. Army Research Laboratory, 2800 Powder Mill Road, Adelphi, MD 20783
1	ATTN: AMSRL-SS
	Director, Benet Weapons Laboratory, LCWSL, USA AMCCOM, Watervliet, NY 12189
1	ATTN: AMSMC-LCB-TL
1	AMSMC-LCB-R
1	AMSMC-LCB-RM
1	AMSMC-LCB-RP
	Commander, U.S. Army Foreign Science and Technology Center, 220 7th Street, N.E., Charlottesville, VA 22901-5396
3	ATTN: AIFRTC, Applied Technologies Branch, Gerald Schlesinger
	Commander, U.S. Army Aeromedical Research Unit, P.O. Box 577, Fort Rucker, AL 36360
1	ATTN: Technical Library
	U.S. Army Aviation Training Library, Fort Rucker, AL 36360
1	ATTN: Building 5906-5907
	Commander, U.S. Army Agency for Aviation Safety, Fort Rucker, AL 36362
1	ATTN: Technical Library
	Commander, Clarke Engineer School Library, 3202 Nebraska Ave., N, Fort Leonard Wood, MO 65473-5000
1	ATTN: Library
	Commander, U.S. Army Engineer Waterways Experiment Station, P.O. Box 631, Vicksburg, MS 39180
1	ATTN: Research Center Library
	Commandant, U.S. Army Quartermaster School, Fort Lee, VA 23801
1	ATTN: Quartermaster School Library
	Naval Research Laboratory, Washington, DC 20375
2	ATTN: Dr. G. R. Yoder - Code 6384
	Chief of Naval Research, Arlington, VA 22217
1	ATTN: Code 471
	Commander, U.S. Air Force Wright Research & Development Center, Wright-Patterson Air Force Base, OH 45433-6523
1	ATTN: WRDC/MLLP, M. Forney, Jr.
1	WRDC/MLBC, Mr. Stanley Schulman

No. of Copies	To
	U.S. Department of Commerce, National Institute of Standards and Technology, Gaithersburg, MD 20899
1	ATTN: Stephen M. Hsu, Chief, Ceramics Division, Institute for Materials Science and Engineering
1	Committee on Marine Structures, Marine Board, National Research Council, 2101 Constitution Avenue, N.W., Washington, DC 20418
1	Materials Sciences Corporation, Suite 250, 500 Office Center Drive, Fort Washington, PA 19034
1	Charles Stark Draper Laboratory, 555 Technology Square, Cambridge, MA 02139
1	Wyman-Gordon Company, P.O. Box 8001, North Grafton, MA 01536-8001
1	ATTN: Technical Library
1	General Dynamics, Convair Aerospace Division, P.O. Box 748, Fort Worth, TX 76101
1	ATTN: Mfg. Engineering Technical Library
	Plastics Technical Evaluation Center, PLASTEC, ARDEC, Bldg. 355N, Picatinny Arsenal, NJ 07806-5000
1	ATTN: Harry Pebly
1	Department of the Army, Aerostructures Directorate, MS-266, U.S. Army Aviation R&T Activity - AVSCOM, Langley Research Center, Hampton, VA 23665-5225
1	NASA - Langley Research Center, Hampton, VA 23665-5225
	U.S. Army Vehicle Propulsion Directorate, NASA Lewis Research Center, 2100 Brookpark Road, Cleveland, OH 44135-3191
1	ATTN: AMSRL-VP
1	Director, Defense Intelligence Agency, Washington, DC 20340-6053
1	ATTN: ODT-5A (Mr. Frank Jaeger)
	U.S. Army Communications and Electronics Command, Fort Monmouth, NJ 07703
1	ATTN: Technical Library
	U.S. Army Communications and Electronics Command, Intelligence and Electronic Warfare Center, Fort Monmouth, NJ 07703-5211
1	ATTN: Frank Elmer, AMSEL-RD-IEW-TAE-M
	U.S. Army Research Laboratory, Electronic Power Sources Directorate, Fort Monmouth, NJ 07703
1	ATTN: AMSRL-EP-M, W. C. Drach
1	AMSRL-EP-M, T. E. Koscica
1	AMSRL-EP-M, R. W. Babbit
	Director, U.S. Army Research Laboratory, Watertown, MA 02172-0001
2	ATTN: AMSRL-OP-WT-IS, Technical Library
25	Authors